Introducing Polyolefins
Content

- Synthetic polymers
  - Classification
  - Global production

- Polyolefins
  - Polyolefins family
  - PE classification
  - PP structures
  - Key properties
  - Additivation
  - Application
  - Global consumption
  - Domestic production and consumption
### Synthetic Polymers Classification by Plastics Europe

<table>
<thead>
<tr>
<th>Category</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Plastics</td>
<td><strong>PE, PP, PVC, PS, EPS, PET</strong> (Bottle grade)</td>
</tr>
<tr>
<td>Engineering Plastics</td>
<td>ABS, SAN, PA, PC, PBT, POM, PMMA, Other High Performance Polymers</td>
</tr>
<tr>
<td>PUR</td>
<td>Polyurethanes</td>
</tr>
<tr>
<td>Thermoplastics</td>
<td><strong>Standard Plastics</strong> + Engineering Plastics</td>
</tr>
<tr>
<td>Plastic Materials</td>
<td><strong>Standard Plastics</strong> + Engineering Plastics + <strong>PUR</strong></td>
</tr>
<tr>
<td>Plastics</td>
<td><strong>Plastic Materials</strong> + Others (Thermosets, Adhesives, Coatings, Sealants)</td>
</tr>
<tr>
<td>Elastomers</td>
<td>Synthetic Elastomers (SBR, IR, IIR, BR, NBR, CR, Others)</td>
</tr>
<tr>
<td>Fibres</td>
<td>PA, Polyester, Acrylic, Other Synthetic Fibres</td>
</tr>
<tr>
<td>Synthetic Polymers</td>
<td><strong>Plastic Materials</strong> + Fibres + Elastomers + Others (Thermosets, Adhesives, Coatings, Sealants)</td>
</tr>
</tbody>
</table>
World Synthetic Polymers Production 2007

- Synthetic Polymers production in 2007 approximately 315 million t globally

- PE+PP represents 114 million t or 36% of global Synthetic Polymers production

**Notes:**

- PUR: Polyurethanes
- Thermoplastics: Standard Plastics+ Engineering Plastics
- Others: Thermosets, Adhesives, Coatings, Sealants
- Elastomers: Synthetic Elastomers (SBR, IR, IIR, BR, NBR, CR, Others)
- Fibres: PA, Polyester, Acrylic, Other Synthetic Fibres

**Graph:**

- Thermoplastics: 65%
  - Polyolefins (PE+PP): 36%
  - Others: 14%
- Fibres: 13%
- Elastomers: 4%
- PUR: 4%
World Plastics Production
1950 – 2011
Plastics=Synthetic Polymers less Elastomers and Fibres
Polyolefins

PE and PP
The Polyolefins Family

Polyethylene - PE
- LDPE
- Linear PE
  - HDPE/MDPE
  - LLDPE

Polypropylene - PP
- Homopolymers
- Copolymers
  - Random copolymers
  - Block copolymers (impact copolymers, heterophase copolymers)
PE Classification by Density

<table>
<thead>
<tr>
<th>DENSITY</th>
<th>COMONOMER</th>
<th>PE GRADE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.926-0.970</td>
<td>–/alfa-Olefins</td>
<td>HDPE</td>
</tr>
<tr>
<td>0.926-0.940</td>
<td>alfa-Olefins</td>
<td>MDPE</td>
</tr>
<tr>
<td>0.915-0.935</td>
<td>–/Acrylates/VA</td>
<td>LDPE</td>
</tr>
<tr>
<td>0.915-0.926</td>
<td>alfa-Olefins</td>
<td>LLDPE</td>
</tr>
</tbody>
</table>

Schematic representation of various PE structures

HDPE/MDPE

LLDPE

LDPE
HDPE Chain Segments
LLDPE Chain Segment
LDPE Chain Segment
PP Structures

Isotactic homopolymer

Atactic homopolymer

Syndiotactic homopolymer

Block copolymer

PPP EEEEEEEE PPPP PEEEEEEEEE PPP

Random copolymer

PPPPPEPPEPPEPPEPPEPPEEPPPEEPPP
Isotactic PP Chain Segment
Atactic PP
Syndiotactic PP
PP Homopolymer and Random Copolymer
PP Block Copolymer
Connection between properties

Primary properties
- molecular weight
- molecular weight distribution
- comonomer content
- stereoregularity (PP)

Secondary or end use properties
- melt index
- mechanicals
  - tensile strength
  - flexural modulus
  - impact strength
- ESCR
Molecular weight

- **Number average**
  
  \[ M_n = \frac{\sum N_i M_i}{\sum N_i} \]

- **Weight average**
  
  \[ M_w = \frac{\sum N_i M_i^2}{\sum (N_i M_i)} \]

- **Polydispersity**
  
  \[ P = \frac{M_w}{M_n} \]
Molecular weight distribution

![Diagram showing molecular weight distribution with number average molecular weight (Mn) and weight average molecular weight (Mw).]
Bimodal Polymer
Molecular structure vs. properties

Low Mw homopolymer:
- increased crystallinity → higher stiffness
- good processability

high Mw copolymer:
- tie chains between crystals
- elastic properties
- high mechanical strength
- high toughness
- excellent ESCR

Comonomer built into high Mw molecules:
- impact strength
- ESCR

SCB/1000C

Mw →

N →
Melt Index

- Melt index – measure of ease of flow of polymer melt
  - One kind of reciprocal viscosity
  - Instead of determination of molecular weight
  - Fast standard method to
    - control quality
    - compare products

- Melt index and molecular weight
  - High melt index = low viscosity = low molecular weight
  - Low melt index = high viscosity = high molecular weight

- Non Newtonian behaviour
  - Melt index (viscosity) depends on load
  - Melt indices measured at different loads give indication on molecular weight distribution
Density (D)

- Important for PE - strong influence on properties
- Depends on comonomer content (SCB=short chain branching): more SCB = lower D
- Longer comonomer chain = lower D
- Comonomers tend to incorporate into lower $M_w$ molecules deteriorating organoleptic properties
Mechanical Properties 1

- **Tensile strength (TS)**
  - Higher crystallinity results in higher TS
  - $TS_{PP} > TS_{HDPE} > TS_{LDPE}$
  - TS measured on both machine (MD) and transversal direction (TD) on film
Mechanical Properties 2

Impact strength (IS)
- Ability to withstand shock loading
- Higher $M_w$ = higher IS
- Lower $D$ = higher IS
- Dart drop: special impact test for film grades
Mechanical Properties 2

- Flexural modulus (FM)
  - Measure of stiffness – higher FM means higher stiffness
  - Higher D = higher FM
  - \( FM_{PPHOMO} > FM_{PPHECO} > FM_{PPRACO} \)
ESCR – Environmental Stress Cracking Resistance

- Ability to withstand cracking under load in chemicals
- Mainly used for PE - very important for blow moulding and pipe grades
- Lower D = higher ESCR
- Higher M_W = higher ESCR
- Role of comonomer distribution – comonomers built into high M_W molecules give very good ESCR
Additivation

Polyolefins mainly PP and HDPE need different additives to meet end use requirements. Typical concentration: some hundreds through some thousands ppm (1 ppm=1 g/t)

Typical polyolefins additives

- **Stabilizers** – to protect polymer from oxidative degradation during
  - Processing – melt stabilization (high temperature, short time + oxygen)
  - Long term use
    - thermal stabilization (low temperature, long time + oxygen)
    - UV stabilization – (low temperature, long time, UV light + oxygen)
- **Processing aids and property modifiers**
  - Slip agents – to reduce friction during processing
  - Antistatic agent – to prevent build up of electrostatic charging
  - Antiblocking agent – to avoid sticking of film layers
  - Nucleating agents – to improve stiffness
  - Clarifying agents – to increase product transparency
Global Consumption

millió tonna


PE
PP
Per Capita Consumption

- North America
- South America
- Western Europe
- Africa
- Asia
- Global

kg per capita

PE
PP
Domestic Production and Consumption

![Graph showing domestic production and consumption over years 2001 to 2012. The graph includes bars for PE production, PE consumption, PP production, and PP consumption.]